Lifetime-Limited Photochemical Hole-Burning in s-Tetrazine-Benzene Mixed Crystals at 2 K

Vries, Harmen de; Wiersma, Douwe A.

Published in:
Chemical Physics Letters

DOI:
10.1016/0009-2614(77)85425-0

Publication date:
1977

LIFETIME-LIMITED PHOTOCHEMICAL HOLE-BURNING IN s-TETRAZINE–BENZENE MIXED CRYSTALS AT 2 K

Harmen DE VRIES and Douwe A. WIERSMA
Laboratory for Physical Chemistry, University of Groningen, Groningen, The Netherlands

Received 12 July 1977

We show that the technique of photochemical hole-burning can be utilized to measure sub-nanosecond fluorescence lifetimes of molecular excited states. s-tetrazine is taken as an example and from the width of the hole (0.7 ± 0.1 GHz), burned in the origin of the lowest $^1B_{3u} \leftarrow {}^1A_{1g}$ transition at 2 K in a benzene mixed crystal, a fluorescence lifetime of 455^{+75}_{-55} ps is obtained. The coherence lifetime of the 16 a_0^2 vibronic transition is found to be 25 ps.

1. Introduction

Recently several reports on homogeneous linewidths [1–3] of $S_1 \leftarrow S_0$ electronic origins (zero phonon lines) in molecular mixed crystals show that at low temperature ($\lesssim 1.5$ K) the contribution of purely phase-destructive events to the homogeneous linewidth is at most a few tens of MHz. One then expects that for short (sub-nanosecond) fluorescence lifetimes the homogeneous linewidth is completely determined by this lifetime. Of course this can be exploited using the photochemical hole-burning method to determine *sub-nanosecond* fluorescence lifetimes of excited states in molecular mixed crystals, which otherwise are only obtainable using picosecond lasers. In the light of recent results of (stimulated) photon-echo measurements on a molecular radical [4] we wish to make a limitation here to molecules which exhibit two-level system behaviour at the laser frequency.

In this letter we report as an example of the method, the results obtained on the $S_1 \leftarrow S_0$ electronic origin of s-tetrazine in a benzene host lattice [5]. s-tetrazine is attractive as a testcase as the sub-nanosecond fluorescence lifetime in a benzene solution at 300 K was previously measured (450 ± 55 ps) using picosecond laser techniques [6]. From the hole-burning experiment at 2 K we would therefore expect to find a similar number. At low temperature s-tetrazine was shown to photodecompose into N_2 and HCN [7] while the photodissociation quantum yield obtained in the gas phase was 1 [5].

We have also performed hole-burning at 2 K on the 16 a_0^2 vibronic transition in the $S_1 \leftarrow S_0$ absorption spectrum of s-tetrazine in benzene [5]. Finally we comment on the different inhomogeneous widths of the electronic and vibronic transitions.

2. Experimental

The mixed s-tetrazine in benzene crystals were prepared as described in ref. [5]. No attempts were made to orient them. During the experiments the crystals were immersed in superfluid helium in a glass dewar.

The results of fig. 1 were obtained using basically the excitation technique described in ref. [1]. In order to prevent burning during probing of the absorption lines, the probing power needed to be reduced so much that the resulting signal-to-noise ratio obtained was very poor. We therefore introduced an acousto-optic modulator (SORO M 30 M) in the laser beam right in front of the sample. The first order beam from the modulator was directed to the sample through attenuating colour glass filters and modulated during probing at 300 Hz. The s-tetrazine emission signal from the photomultiplier was then detected using a lock-in amplifier. Burning during probing was further prevented by scanning the dye laser relatively fast, about 200

MHz/s, across the absorption profile. The excitation spectra of the 5801.8 Å origin and the 5632.0 Å vibronic line were obtained through detection of the emission band at 6057 Å [5] using a $\frac{1}{2}$m Jarrell–Ash monochromator. The average absorption probe power for the 5801.8 Å line was 0.1% of the 10 mW burning power and for the 5632.0 Å line ca. 3% of the 50 mW burning power.

3. Results

In fig. 1b a high-resolution scan of the origin absorption line at 5801.8 Å is shown to have a gaussian lineshape with 24.2 ± 1 GHz fwhm. From this lineshape we conclude that this line is mainly inhomogeneously broadened. This is confirmed by the hole-burning experiment on this transition. The hole burned was persistent at 2 K for at least the time of the experiment (≈4 h). Fig. 1c shows a high-resolution tracing of this hole and its width is measured to be 0.8 ± 0.1 GHz. For the hole-width extrapolated to zero burning time we find 0.7 ± 0.1 GHz. Since the effective laser linewidth during the burning time is only a few percent of this hole-width we will ignore its contribution in the calculation of the homogeneous width.

In fig. 1d a high-resolution scan of the vibronic absorption line at 5632.0 Å, in contrast to the origin, is shown to have a lorentzian lineshape with 14.2 ± 1 GHz fwhm. From this one would conclude that this line is mainly homogeneously broadened. The hole-burning experiment confirms this assumption: after burning this absorption line is decreased as a whole (fig. 1d). Note that these hole-burning results for s-tetrazine are qualitatively similar to those obtained for dimethyl s-tetrazine [1]‡.

Further note in figs. 1b and 1d the marked difference in *inhomogeneous* width of the origin and the vibronic transition.

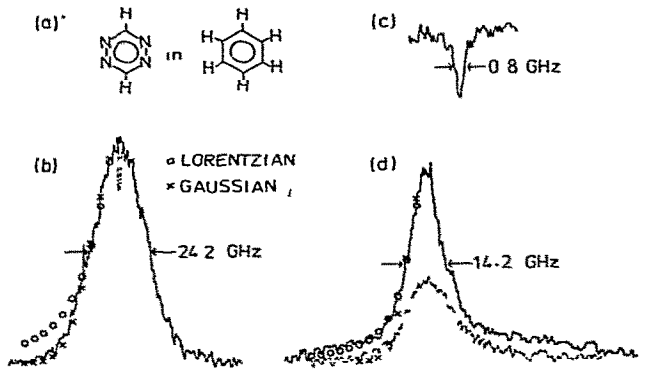

Fig. 1. cw-dye-laser-induced excitation (absorption) spectra of (b) the origin at 5801.8 Å and (d) the vibronic transition at 5632.0 Å of s-tetrazine in benzene (a) at 2 K. The dye-laser was scanned through the absorption regions with instantaneous bandwidth (≈ resolution) of < 20 MHz. The dotted spectra were obtained after 5 s burning (effective bandwidth 35 MHz) in the origin and 15 s burning (effective bandwidth 35 MHz) in the vibronic line (at the top). (c) High-resolution scan of the hole burned in the origin.

4. Discussion

To obtain the homogeneous linewidth of the origin from the hole-width we proceed as follows. In the limit of zero burning time we may in our case apply the hole-burning theory of Sargent III and Toschek [8,9] where we only have to consider the incoherent absorption coefficient α_{inc}. For $\mathrm{Em}(\nu)$, the emission detected as a function of laser frequency ν, we have, when Beer's law applies,

$$\mathrm{Em}(\nu) \propto I_0 \, (1 - \mathrm{e}^{-\alpha(\nu) z}) \, ,$$

where I_0 is the intensity incident on the sample and z is the length of the exciting light path through the sample. When $\alpha(\nu)\, z \ll 1$, as is appropriate in our case, we get $\mathrm{Em}(\nu) \propto \alpha(\nu) z$. This means that for the hole detected in emission we can use the expression for α of Sargent III and Toschek (eq. (17) of ref. [9]). We then obtain for the hole-width (fwhm):

$$\Delta\omega = 2\pi\Delta\nu = (2/T_2) \{1 + [1 + E_{sat}^2 (\mu/\hbar)^2 \, T_1 \, T_2]^{1/2}\} \, ,$$

where T_1 is the longitudinal and T_2 the transverse relaxation time in the optical analog of the Bloch equations [10]. E_{sat} is the electric field amplitude of the saturating beam, μ is the electric-dipole matrix element and $\hbar$ is Planck's constant/2π. When power broadening is negligible, which we assume to be the case, one can

‡ Recently we repeated the hole-burning experiments on the 5875 Å origin of DMST in durene at 1.8 K with a frequency stabilized (within 2 MHz over 5 s) and intensity stabilized (to better than 0.5%, bandwidth 150 kHz) Spectra-Physics 580 A dye laser. The results gave a homogeneous linewidth of 24 ± 5 MHz which is completely determined by the 6 ns lifetime.

easily see that the hole-width $\Delta\nu$ (fwhm) is twice the homogeneous width $1/\pi T_2$. We incidentally note here that this result, without comment, was also used in our first report on photochemical hole-burning [1]. From the hole-width in s-tetrazine we then calculate a homogeneous linewidth of 350 ± 50 MHz. As this width most certainly is only due to a T_1 process, which implies $1/\pi T_2 = 1/2\pi T_1$, we calculate $T_1 = 455^{+75}_{-55}$ ps. It is gratifying to note that the lifetime calculated from the photochemical hole-burning is identical to the one measured in solution at 300 K [6]. The usefulness of the photochemical hole-burning method in determining sub-nanosecond fluorescence lifetimes is hereby clearly demonstrated.

Consider now the 5632.0 Å lineshape and linewidth. Above it was concluded from the hole-burning result that this line is mainly homogeneously broadened. From Voigt simulations of the lineshape using Posener's tables [11] we conclude that the homogeneous linewidth of this transition is larger than 9.5 GHz. Thus we have 9.5 GHz $< 1/\pi T_2 <$ 14.2 GHz or for the coherence lifetime 22.4 ps $< T_2 <$ 33.5 ps.

From the Voigt analyses it follows that the inhomogeneous width of the vibronic line is smaller than 8 GHz. Compared to the 24.2 GHz origin inhomogeneous width this is a rather remarkable result. Furthermore 0.1 cm^{-1} resolution absorption spectra of several singlet vibronic lines of s-tetrazine in benzene at 1.8 K show large variations in linewidths [12]. Obviously more experiments need to be done to clarify these differences in inhomogeneous and homogeneous linewidths.

In conclusion we remark here that from spectra of different sites in mixed crystals [13] one also can infer that electronic and vibronic transitions of one site can have different inhomogeneous widths; the recent experiments of Gorokhovski and Kikas [14] further confirm this point.

Acknowledgement

We are indebted to the Netherlands Foundation for Chemical Research (S.O.N.) for generous financial support of this investigation.

References

[1] H. de Vries and D.A. Wiersma, Phys. Rev. Letters 36 (1976) 91.
[2] T.J. Aartsma and D.A. Wiersma, Chem. Phys. Letters 42 (1976) 520;
J.B.W. Morsink, T.J. Aartsma and D.A. Wiersma, Chem. Phys. Letters 49 (1977) 34.
[3] S. Volker and J.H. van der Waals, Mol. Phys. 32 (1976) 1703;
S. Volker, R.M. MacFarlane, A.Z. Genack H.P. Trommsdorff and J.H. van der Waals, J. Chem. Phys., to be published.
[4] W.H. Hesselink and D.A. Wiersma, Chem. Phys. Letters 50 (1977) 51.
[5] J.H. Meyling, R.P. van der Werf and D.A. Wiersma, Chem. Phys. Letters 28 (1974) 364.
[6] R.M. Hochstrasser, D.S. King and A.C. Nelson, Chem. Phys. Letters 42 (1976) 8.
[7] R.M. Hochstrasser and D.S. King, J. Am. Chem. Soc. 98 (1976) 5443.
[8] M. Sargent III, P.E. Toschek and H.-G. Danielmeyer, Appl. Phys. 11 (1976) 55.
[9] M. Sargent III and P.E. Toschek, Appl. Phys. 11 (1976) 107.
[10] F. Bloch, Phys. Rev. 70 (1946) 460.
[11] D.W. Posener, Australian J. Phys. 12 (1959) 184.
[12] J.H. Meyling and D.A. Wiersma, unpublished results.
[13] R.M. Hochstrasser and P.N. Prasad, Chem. Phys. Letters 8 (1971) 315.
[14] A.A. Gorokhovski and J. Kikas, Opt. Commun. 21 (1977) 272.